5-11 was applied. Two peaks corresponding to **14** and **15** were observed at the respective ratio of 6:94.

HPLC Analysis of Irradiated Samples of 19-22. The solution of **19** in MeOH (5.5×10^{-4} M) before and after irradiation were analyzed on HPLC with a reversed-phase column (TSK gel ODS-120A). While a gradient elution (20% CH_3CN–50% CH_3CN, 1 mL/min, 1 min/%) was applied at 35 °C, the UV absorption at 221 nm was monitored. The same procedure was used for analyses of **20-22** except for the use of DMF in place of MeOH for **22** as the solvent of the sample solution due to solubility problem. The HPLC peak positions of these substances before irradiation were 46.0, 44.3, 41.7, and 36.9% CH_3CN for **19**, **20**, **21**, and **22**, respectively. The elution order of these substances became opposite after irradiation as shown by the peaks positioned at 24.8, 30.8, and 31.7% CH_3CN for **20**, **21**, and **22**, respectively. No peak was observed for the photodimer of **19** due to its short life-time.

Hydrolysis of Irradiated Samples of 19-22. The solution of **22** in MeOH (5 mL, 1.0×10^{-4} M) was irradiated for 1 h, and the solvent was removed under reduced pressure. To the solid residue was added a 4 N NaOH solution, and the solution was stirred overnight. The reaction mixture was neutralized with a HCl solution (4 N) and injected into a HPLC column (ODS-120A). A solution composed of 45% CH_3CN and 55% buffer (0.2 M $Et_3N{\cdot}H_3PO_4$, pH 3) was used as eluent. The same procedure was used for hydrolysis of **19-21**.

Photodimerization of 9-Anthracenecarboxylic Acid. A mixture of 9-anthracenecarboxylic acid (40 mg) and MeOH (20 mL) was irradiated for 6 h under nitrogen, and then the solvent was removed under reduced pressure. Silica gel column chromatography with *n*-hexane/ether/AcOH (75:25:1 and 50:50:1) gave the photodimer (30%): NMR (DMSO-d_6) δ 5.62 (s, 2 H), 6.75-6.90 (m, 16 H).

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Intramolecular Cyclopropanation Reaction of Furanyl Diazo Ketones

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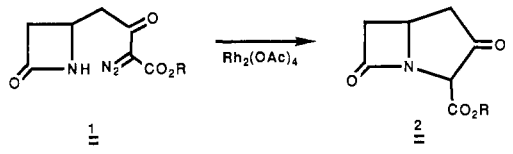
α-Diazo ketones derived from furanyl- and benzofuranylpropionic acids were prepared, and their rhodium(II) acetate catalyzed behavior was studied. The results are consistent with a mechanism in which the key step involves addition of a keto carbenoid intermediate on to the furanyl π-bond followed by an electrocyclic ring-opening reaction. In the case of the benzo-substituted furanyl system, the suspected bicyclic intermediate was isolated in high yield and its chemistry was subsequently investigated. The bicyclic ketone derived from 1-diazo-4-(2-benzofuryl)-2-butanone undergoes a novel thermal rearrangement to a benzopyranone derivative. This unexpected transformation can be rationalized in terms of a [4 + 2]-cycloreversion reaction to give an ortho-quinoidal intermediate, which undergoes a subsequent electrocyclic ring closure followed by a 1,3-hydrogen shift. Furans with side chains of various lengths containing a diazomethyl keto group were also studied. The cyclization chemistry of the closely related diazothienylalkanone system was investigated and found to give products derived from an analogous intramolecular cyclopropanation reaction.

α-Diazo carbonyl compounds have been widely studied under thermal, photochemical, and transition metal catalyzed conditions.[1,2] Intramolecular cyclization of α-carbonyl carbenes and carbenoids derived from α-diazo ketones has found widespread application for the preparation of a variety of theoretically and biologically interesting compounds.[3-11] Probably one of the more significant insertion reactions of recent years is outlined below



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and represents the key step in the Merck synthesis of carbapenams.[12,13] Since rhodium-catalyzed decomposition of diazo ketones involves a rhodium carbenoid intermediate rather than a free carbene,[14,15] the above type of ring closure is probably better regarded as nucleophilic attack by the lactam NH on the rhodium carbenoid, rather than an insertion into the NH bond.

Transition metal mediated intramolecular additions to π-bonds have also been extensively utilized in carbocyclic synthesis. A general review of intramolecular diazo carbonyl reactions appeared in 1979,[2] and since then, many further publications on transition metal catalyzed reactions

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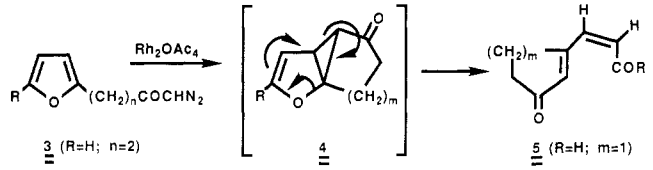
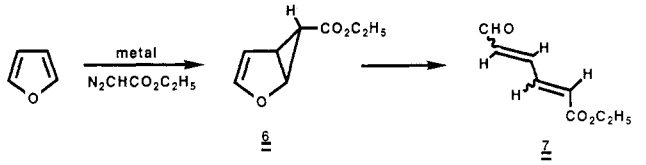
have extended the scope of this methodology.[16,17] Elegant and practical examples of this reaction include the syntheses of gibberellin/gibberellic[18] acid and the triquinane sesquiterpenes.[19] Aside from Scott's synthesis of azulene,[20] however, few other intramolecular keto carbene additions to aromatic rings have been reported.[21] The ease with which α-carbonyl carbenoids add to furans[22,23] suggested that the intramolecular version of this reaction should also occur. This idea was lent credence by a 1974 report describing the copper sulfate induced reorganization of diazo ketone **3** to cyclopentenone **5**.[24]



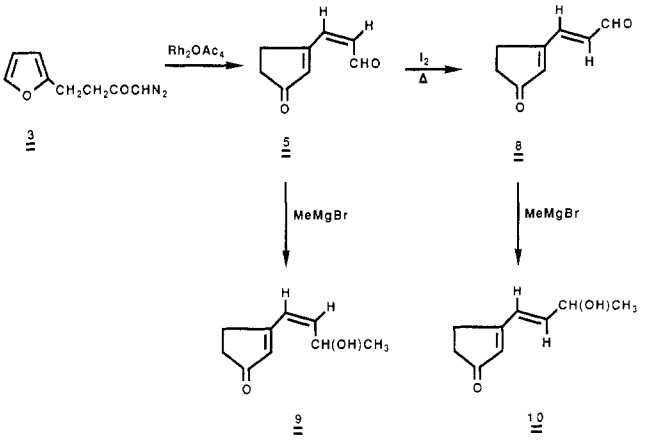
We thought that this reaction could be of further synthetic value as it permits for the synthesis of a complex cyclopentenone in a single step. Thus, we became interested in exploring the potential of the rhodium carbenoid induced intramolecular cycloaddition to furans as a general route to cycloalkenones.[25,26] In this paper we present results that show that the reaction of α-diazo ketones derived from furanyl- and benzofuranylpropionic acids with rhodium(II) acetate leads to cycloalkenones in high yield. Mechanistically, the reaction involves addition of the keto carbene to the furanyl π-bond followed by an electrocyclic ring-opening reaction.[27]

Results and Discussion

The bimolecular reaction of α-diazo carbonyl compounds with aromatic molecules has received much attention.[28] In most instances, the reaction is catalyzed by transition metals and involves the loss of nitrogen to produce a carbenoid intermediate, which adds across the aromatic π-system to give a cyclopropane adduct.[29-31] The resulting norcaradiene intermediate subsequently tautomerizes to a cycloheptatriene. Polynuclear aromatic and π-excessive heteroatoms containing oxygen or sulfur atoms generally undergo cyclopropanation with cleavage as illustrated below.[22-26]



The recent switch from copper to rhodium-based catalysts has produced major improvements in both intermolecular and intramolecular cycloaddition reactions of diazo carbonyl compounds with aromatic systems.[15,32] Not only are yields significantly higher with rhodium catalysts, but the reaction conditions are frequently mild enough to permit isolation of transient intermediates. In seeking to develop a general synthetic entry into the 3-vinylcycloalkenone series for eventual Diels–Alder chemistry, we have reinvestigated the rhodium-catalyzed reaction of the α-diazo ketone **3** derived from 2-furanpropionic acid. α-Diazo ketone **3** had previously been reported to afford *trans*-cyclopentenone **8** in 60% yield when exposed to copper sulfate in refluxing cyclohexane. We found that treatment of **3** with a catalytic quantity of rhodium(II) acetate in methylene chloride at 25 °C afforded a crystalline keto aldehyde (i.e., **5**) in 86% yield, which was identical in all respects with the compound reported by Nwaji and Onyiriuka.[24] The spectral data of the keto



aldehyde (NMR ($CDCl_3$, 90 MHz) δ 2.57 (t, 2 H, J = 5.0 Hz), 2.95 (t, 2 H, J = 5.0 Hz), 6.21 (dd, 1 H, J = 13.0 and 8.0 Hz), 6.33 (s, 1 H), 7.21 (d, 1 H, J = 13.0 Hz), and 10.19 (d, 1 H, J = 8.0 Hz)) and its ready conversion to **8** by treatment with iodine in benzene showed that the initial structure possesses the *Z* configuration in the side chain. All attempts to detect an oxabicyclo[3.1.0]hex-2-ene intermediate (i.e., **4**) failed. Reaction of keto aldehyde **5** (or **8**) with methylmagnesium bromide proceeded exclusively at the aldehydic terminus to give keto alcohol **9** (or **10**).

A similar reaction of diazo ketone **11** at 25 °C for 3.5 h converted it to (*Z*)-1-(3-oxo-1-cyclopentenyl)-1-buten-3-one (**12**) in 87% isolated yield. Thus, substitution on the furan

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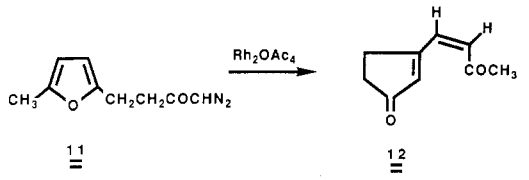
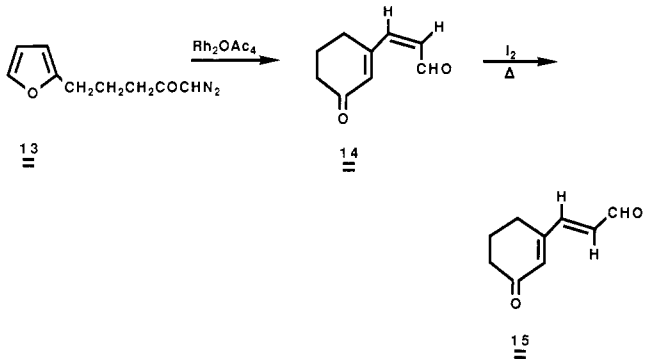
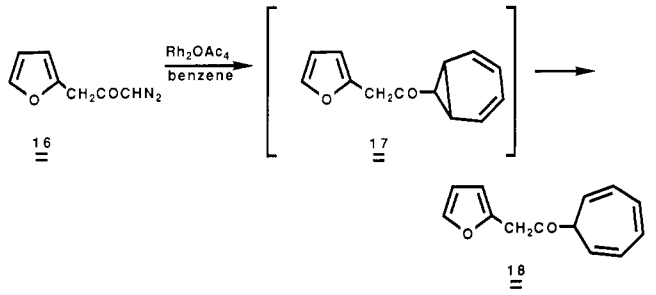


ring has no ill effect on the synthetic method.

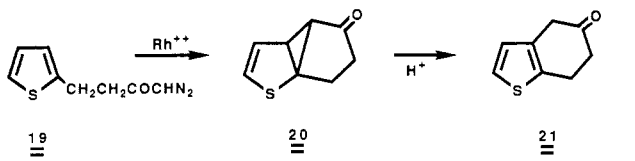
We have also studied the rhodium-catalyzed reaction of the homologous furan diazo ketone **13** in order to ascertain the effect of ring size on the cyclization reaction. Exposure of **13** to the rhodium(II) catalyst at 25 °C for 3 h afforded the *Z* keto aldehyde **14** (87%), which could readily be transformed into the *E* isomer **15** by heating with iodine in benzene.



The same reaction with the lower homologue **16** in methylene chloride yielded a complex mixture of products. When benzene was used as the solvent, however, cycloheptatrienyl ketone **18** was formed in 68% yield as the only isolable product. It seems reasonable to assume that, in this case, intramolecular addition of the rhodium carbenoid to the furan ring does not take place as a consequence of the high strain energy of the bicyclopentanone intermediate. Instead, bimolecular addition to benzene occurs to give a norcaradiene intermediate (i.e., **17**), which subsequently tautomerizes to produce ketone **18**.

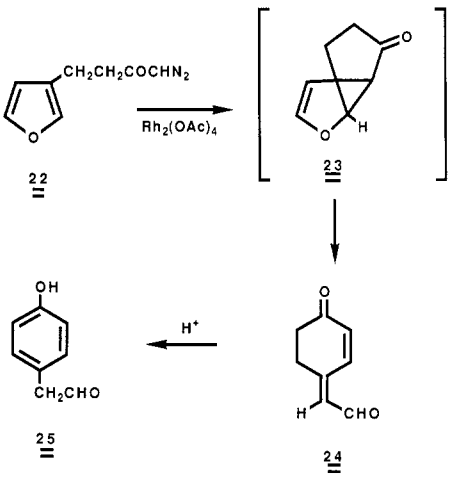


In order to ascertain the effect of the heteroatom on the cyclization reaction, the decomposition of thienyl diazo ketone **19** was investigated. Interestingly, the suspected bicyclo[3.1.0]hex-2-ene intermediate (i.e., **20**) could actually



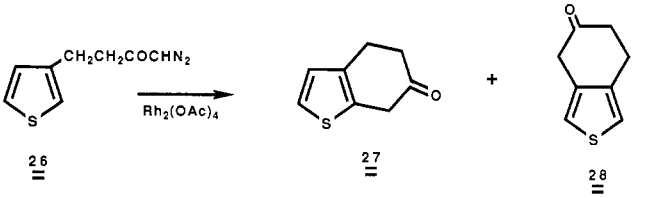
be isolated in high yield (NMR ($CDCl_3$, 90 MHz) δ 1.16 (s, 1 H), 2.12 (br t, 2 H, J = 7.0 Hz), 2.44 (t, 1 H, J = 7.0 Hz), 2.56 (t, 1 H, J = 7.0 Hz), 2.92 (br t, 1 H, J = 2.0 Hz), 5.89 (dd, 1 H, J = 6.0 and 2.0 Hz), and 6.27 (d, 1 H, J = 6.0 Hz)). Attempts to purify **20** by silica gel chromatography resulted in the formation of the rearranged benzothiophen-5(4*H*)-one **21** in 68% yield. The cyclization of the thienyl diazo ketone **19** is remarkable in that the sole product formed corresponds to tricyclic ketone **20**. This result is strikingly different from that encountered in the furan system where the initially formed cycloadduct (i.e., **4**) is rapidly unravelled to the cyclopentenone derivative. The difference in reactivity between **4** and **20** may be attributed to the stronger C=O double bond that is formed in the [4+2]-cycloreversion reaction and which apparently facilitates the rearrangement.

Since we were interested in the synthetic utility of the cyclization reaction, we undertook a study of the decomposition of the closely related 3-furanyl-substituted diazo ketone **22**. Addition of rhodium(II) acetate to a solution of **22** in benzene produced an efflux of nitrogen gas and



provided *cis*-(4-oxo-2-cyclohexen-1-ylidene)acetaldehyde (**24**) in 88% yield: NMR ($CDCl_3$, 360 MHz) δ 2.65 (t, 2 H, J = 5.0 Hz), 2.90 (t, 2 H, J = 5.0 Hz), 6.14 (d, 1 H, J = 7.0 Hz), 6.29 (d, 1 H, J = 10.0 Hz), 8.01 (d, 1 H, J = 10.0 Hz), and 10.14 (d, 1 H, J = 7.0 Hz). Chemical support for the structure of **24** was obtained by its acid-catalyzed rearrangement to *p*-hydroxyphenylacetaldehyde (**25**). The formation of **24** can be rationalized by assuming intramolecular keto carbene addition to the furan π-bond to give **23**, which is rapidly converted to **24** via a [4+2]-cycloreversion reaction.[22,33] Isolation of the acid-labile species **24** is a clear testimonial to the mildness of the conditions employed in this chemistry.

We also studied the cyclization chemistry of the closely related 1-diazo-4-(3-thienyl)-2-butanone (**26**) system and encountered different results. Exposure of **26** to $Rh_2(OAc)_4$ in benzene at 25 °C for 2 h produced a 6:1 mixture of two compounds, which could readily be separated by silica gel chromatography. The major product was assigned as 4,5-dihydrobenzo[*b*]thiophen-6(7*H*)-one (**27**) while the minor component corresponded to 6,7-dihydrobenzo[*c*]-thiopen-5(4*H*)-one (**28**).



The structures of the products rest largely upon the interpretation of the ^{13}C and ^{1}H NMR spectra (see Ex-

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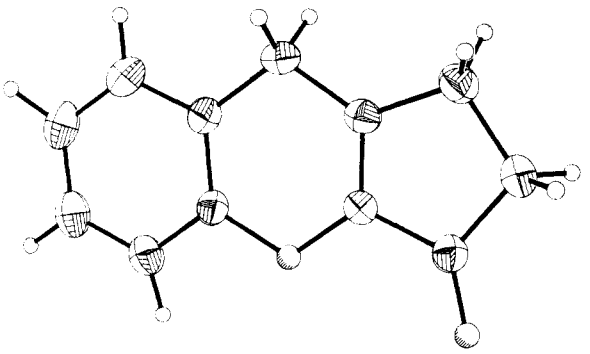
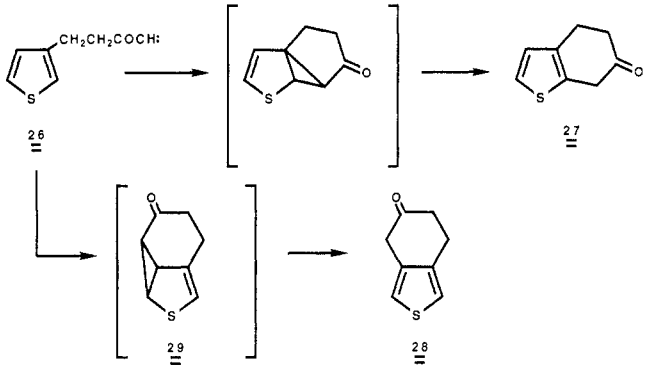
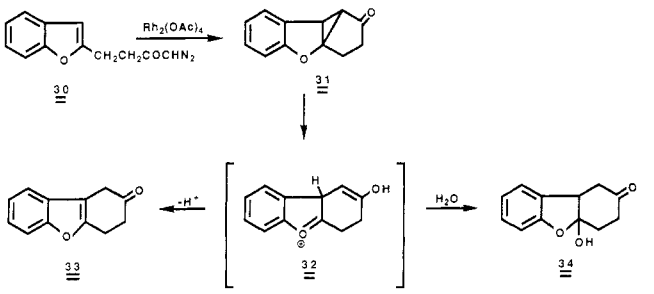


Figure 1. X-ray crystal structure of 1,2-dihydrocyclopenta-[*b*][1]benzopyran-3(9*H*)-one (**37**).

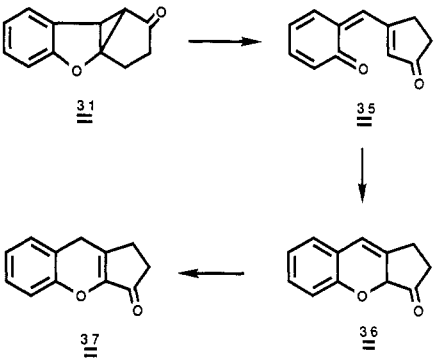
perimental Section). The assignment of structure **27** is consistent with the observed 5.0-Hz coupling constant of the thiophene ring protons whereas **28** showed a singlet for these hydrogens. Formally, the products are the result of insertion by the carbenic carbon into the 2- and 4-positions of the heterocyclic ring. More than likely the formation of **27** involves intramolecular carbenoid addition across the 2,3-π-bond followed by cyclopropyl ketone ring opening as was found with tricycle **20**. The minor product can be rationalized in terms of a carbenoid addition across the 4,5-π-bond. The resulting tricycle **29** is converted to **28** by a subsequent ring-opening reaction. An alternative, but less likely, option involves C–H insertion onto the 4-position of the thiophene ring.



Extension of the carbenoid cycloaddition–rearrangement sequence to the related diazo benzofuran system was next investigated. To this end, diazo ketone **30** was prepared and treated with rhodium(II) acetate at 25 °C. Under these conditions, cyclopropyl ketone **31** could be isolated in 71% yield as a crystalline solid, mp 99–100 °C. Treatment of **31** with a 1% sulfuric acid solution produced dihydrobenzofuranone **33** in excellent yield. Stirring **31** with a 5% sulfuric acid solution, on the other hand, resulted in the isolation of hydroxytetrahydrobenzofuranone **34**. This product is the result of trapping of cation **32** with water rather than by proton loss as was observed at the lower pH. Structure **34** was readily converted to **33** by reaction with thionyl chloride in pyridine.

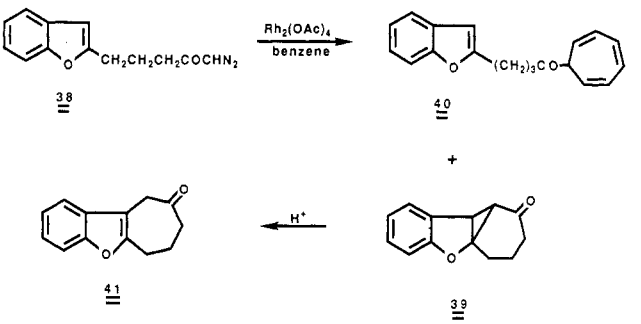


The thermal behavior of **31** presents an interesting contrast to the acid-catalyzed rearrangement. On heating of a sample of **31** at 180 °C for 7 h, a novel rearrangement occurred, producing benzopyranone **37** in 82% yield. The proton NMR spectrum of **37** was deceptively simple, exhibiting a singlet at δ 2.51 for four protons as well as a singlet (2 H) for the benzylic hydrogens at δ 3.72. Unequivocal proof for structure **37** is derived from a single-



crystal X-ray structure analysis. The intensity data were measured on a Nicolet R_3 four-circle diffractometer using Cu Kα radiation. The structure was derived by using direct methods and refined by least squares to give a R value of 0.0366 for all the data. The overall geometry of the molecule is shown in Figure 1. The unexpected conversion of **31** to **37** can be rationalized in terms of a ring-cleavage reaction to give the ortho-quinoidal intermediate **35**, which undergoes a subsequent electrocyclic ring closure followed by a 1,3-hydrogen shift, which is probably acid catalyzed.

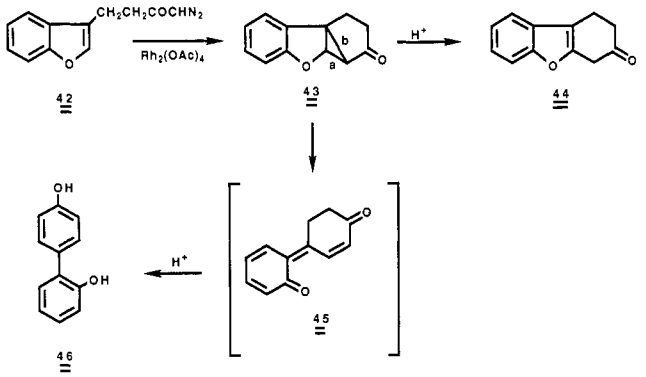
In view of the stringent spatial requirements associated with intramolecular cycloaddition reactions, we thought it worthwhile to consider what effect ring size would have on the cyclization reaction. Toward this end we studied the rhodium(II) acetate induced decomposition of 1-diazo-5-(2-benzofuryl)-2-pentanone (**38**). Exposure of diazoketone **38** to the rhodium catalyst in benzene afforded a mixture of two products. The major product formed



corresponds to cycloheptatriene **40** (56%) derived from a bimolecular addition of the rhodium carbenoid to benzene followed by ring tautomerization. The minor product (38%) is derived by addition of the keto carbenoid intermediate across the furanyl π-bond. This assignment is supported by the acid-induced conversion of **39** to cycloheptabenzofuranone **41**. The formation of a mixture of products in this case indicates that the additional methylene group in **38** has sufficiently retarded the rate of intramolecular addition so as to allow the bimolecular reaction to occur. A similar observation has also been made by Wenkert and co-workers, who found that the most efficient cyclization reaction of 2-(diazoacyl)furans occurs with the cyclopentenone-producing diazo ketone **3**.[26] Structure **39** was the only product isolated (79%) when

the reaction was carried out in methylene chloride.

We also undertook an investigation of the closely related 3-benzofuranyl diazo ketone **42**. Decomposition of **42** and intramolecular cycloaddition of the resulting carbenoid were efficiently accomplished by using the conventional rhodium(II) acetate protocol. This led to the formation of the internal cycloadduct **43** in 91% yield. Treatment



of **43** with a catalytic amount of acid afforded dihydrobenzofuranone **44** in high yield. In recent years there has been considerable interest in the mode of cleavage of cyclopropyl ketones with electrophilic reagents.[34-40] Ring opening of an unsymmetrical, conjugated cyclopropyl ketone has been shown to be a highly stereospecific process in rigid systems.[41,42] It is generally found that rupture occurs at the cyclopropane bond that has maximum overlap with the π-orbital of the carbonyl group. Examination of molecular models indicates that, on this basis, the cyclopropane linkage favored for an acid-induced scission is the exterior one (i.e., bond a). Cleavage of the interior bond (bond b) would violate the stereoelectronic principle formulated by Norin and Dauben,[41,42] since this linkage is aligned almost orthogonally to the π-system of the carbonyl group. Thus, the isolation of **44** is somewhat surprising since its formation requires ring opening of the interior bond. One possible explanation is that **44** is actually formed by cleavage of the exterior bond to give a transient spiro cation, which then undergoes a subsequent Wagner–Meerwein rearrangement. Reversible 1,2-group migrations that interconvert spiro and fused ring systems are known and provide reasonable analogy for this suggestion.[43-45] Unfortunately, a clear distinction between these two options is not possible without labeling studies.[46] Cyclopropyl ketone **43** was also found to undergo a clean thermal rearrangement to biphenyldiol **46**. The formation of **46** probably proceeds via the intermediacy of **45**, which then undergoes a series of hydrogen shifts to give the fully aromatized system.

In conclusion, the facility with which the rhodium-catalyzed cyclopropanation of furanyl diazo ketones occurs makes this reaction particularly attractive for the preparation of highly functionalized cycloalkenones. The creation of complex enones in a single step from simple furan derivatives can be expected to find application in the synthesis of naturally occurring compounds. We are continuing to explore the scope and mechanistic details of these intramolecular cyclopropanation reactions of furanyl diazo ketones and will report additional findings at a later date.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on a Varian EM-390 and a Nicolet NMC-360 MHz spectrometer. ^{13}C NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Rhodium(II) Acetate Catalyzed Reorganization of 1-Diazo-4-(2-furyl)-2-butanone (3). To a stirred solution containing 11.0 g of 2-furanpropionic acid in 200 mL of methylene chloride under a dry nitrogen atmosphere was added 14.2 g of freshly distilled thionyl chloride. The mixture was heated at reflux for 3 h, and the solvent was removed under reduced pressure. Vacuum distillation of the crude mixture gave 9.8 g of 2-furanpropionyl chloride (78%): bp 60–61 °C (0.5 mm); NMR (CCl_4, 90 MHz) δ 3.04 (t, 2 H, J = 6.0 Hz), 3.20 (t, 2 H, J = 6.0 Hz), 6.19 (dd, 1 H, J = 3.0 and 2.0 Hz), 6.42 (d, 1 H, J = 3.0 Hz), and 7.25 (d, 1 H, J = 2.0 Hz); IR (neat) 2960, 1800, 1610, 1510, 1440, 1410, 1345, and 1270 cm^{-1}.

A solution containing 9.8 g of this material in 100 mL of anhydrous ether was added dropwise with stirring to 600 mL of a 0.25 N solution of diazomethane in ether at 0 °C. The mixture was stirred at room temperature for 12 h under a nitrogen atmosphere. Removal of the solvent under reduced pressure gave 9.8 g of a crude yellow oil, which was further purified by column chromatography on silica gel using a 30% ether–hexane mixture as the eluent to give 8.3 g of pure material, which was identified as 1-diazo-4-(2-furyl)-2-butanone (**3**)[24] on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 2.57 (t, 2 H, J = 5.0 Hz), 2.88 (t, 2 H, J = 5.0 Hz), 5.38 (s, 1 H), 5.96 (dd, 1 H, J = 3.0 and 1.0 Hz), 6.20 (d, 1 H, J = 3.0 Hz), and 7.23 (d, 1 H, J = 1.0 Hz); IR (neat) 3140, 2940, 2130, 1640, 1510, 1370, 1140, and 1005 cm^{-1}.

A mixture containing 350 mg of **3** and 4 mg of rhodium(II) acetate in 50 mL of methylene chloride was stirred at 25 °C for 30 min under a nitrogen atmosphere. The inorganic salts were removed by filtration, and the filtrate was concentrated under reduced pressure to give 213 mg (86%) of *cis*-3-(3-oxo-1-cyclopentenyl)-2-propenal (**5**) as an air-sensitive yellow solid: mp 65–66 °C (lit.[24] mp 65 °C); NMR ($CDCl_3$, 90 MHz) δ 2.57 (t, 2 H, J = 5.0 Hz), 2.95 (t, 2 H, J = 5.0 Hz), 6.21 (dd, 1 H, J = 13.0 and 8.0 Hz), 6.33 (s, 1 H), 7.21 (d, 1 H, J = 13.0 Hz), and 10.19 (d, 1 H, J = 8.0 Hz); IR (KBr) 3130, 2950, 1705, 1680, 1580, 1450, 1395, 1295, 1195, 1175, 1130, and 985 cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 31.72, 35.69, 133.63, 134.23, 137.19, 140.54, 190.32, and 207.92.

A solution containing 300 mg of **5** in 50 mL of benzene containing 10 mg of iodine crystals was heated at 80 °C for 42 h. The solvent was removed under reduced pressure to give 300 mg of *trans*-3-(3-oxo-1-cyclopentenyl)-2-propenal (**8**): mp 112–113 °C; IR (KBr) 3130, 2950, 1705, 1580, 1450, 1385, 1295, 1195, 1175, 1130, and 985 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.54 (t, 2 H, J = 5.0 Hz), 2.88 (br t, 2 H, J = 5.0 Hz), 6.46 (s, 1 H), 6.53 (dd, 1 H, J = 17.0 and 7.0 Hz), 7.61 (d, 1 H, J = 17.0 Hz), and 9.77 (d, 1 H, J = 7.0 Hz); UV (95% ethanol) 275 nm (ϵ 40 200); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 26.98, 35.00, 133.64, 137.07, 137.18, 144.35, 192.69, and 208.14. Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.47; H, 5.94.

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(46) A referee has suggested that the rearrangement of **43** to **44** has an analogy in the indole field. Bond b should be properly aligned with the benzylic bond. Invoking a through-ring enol participation could rationalize its cleavage. It is possible that these processes are thermodynamically controlled since an extended aromatic system is being formed.

Reaction of *cis*-3-(3-Oxo-1-cyclopentenyl)-2-propenal (5) with Methylmagnesium Bromide. To a stirred solution containing 350 mg of **5** in 50 mL of dry tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 1 mL of a 2.4 M solution of methylmagnesium bromide in ether. The mixture was stirred at −78 °C for 2.5 h and was then quenched with 50 mL of a 1:1 tetrahydrofuran–saturated aqueous ammonium chloride solution. The mixture was extracted with three 50-mL portions of ether, and the combined extracts were dried over magnesium sulfate and concentrated under reduced pressure. The residue obtained was purified by preparative silica gel thick-layer chromatography using ether as the eluent. The major fraction contained 240 mg (62%) of a clear oil, which was identified as *cis*-1-(3-oxo-1-cyclopentenyl)-1-buten-3-ol (**9**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 1.30 (d, 3 H, J = 7.0 Hz), 2.42 (td, 2 H, J = 5.0 and 2.0 Hz), 2.70–2.90 (m, 2 H), 3.51 (br s, 1 H), 4.81 (qd, 1 H, J = 7.0 and 6.0 Hz), 5.91 (dd, 1 H, J = 12.0 and 6.0 Hz), 6.02 (s, 1 H), and 6.17 (d, 1 H, J = 12.0 Hz); IR (neat) 3400 (br), 2980, 2940, 1710, 1680, 1600, 1510, 1450, 1420, 1295, 1250, 1200, 1120, 1065, and 890 cm^{-1}; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.21, 35.00, 65.62, 123.82, 132.24, 143.51, 171.07, and 209.50. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.96; H, 7.86.

Reaction of *trans*-3-(3-Oxo-1-cyclopentenyl)-2-propenal (8) with Methylmagnesium Bromide. To a stirred solution containing 272 mg of *trans*-3-(3-oxo-1-cyclopentenyl)-2-propenal (**8**) in 50 mL of dry tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 0.83 mL of a 2.4 M solution of methylmagnesium bromide in ether. The mixture was stirred at −78 °C for 2 h and was then quenched with 50 mL of a 1:1 tetrahydrofuran–saturated ammonium chloride solution. The organic layer was removed under reduced pressure, and the mixture was extracted with ether, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was purified by silica gel preparative thick-layer chromatography using ether as the eluent. The major fraction contained 186 mg (69%) of *trans*-1-(3-oxo-1-cyclopentenyl)-1-buten-3-ol (**10**) as a clear oil, whose structure was assigned on the basis of its spectral properties: IR (neat) 3400, 2800, 2700, 1710, 1680, 1640, 1590, 1440, 1390, 1290, 1240, 980, 880, and 760 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.29 (d, 3 H, J = 6.0 Hz), 2.37 (t, J = 6.0 Hz), 2.6–2.9 (m, 3 H), 4.42 (q, 1 H, J = 6.0 Hz), 5.94 (s, 1 H), 6.21 (dd, 1 H, J = 15.0 and 6.0 Hz), and 6.63 (d, 1 H, J = 15.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 23.04, 27.01, 34.69, 67.80, 124.57, 130.62, 142.49, 171.74, and 209.55. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.83; H, 7.72.

Rhodium Acetate Catalyzed Reaction of 1-Diazo-4-(2-(5-methylfuryl))-2-butanone (11). A solution containing 8.0 g of 3-(2-(5-methylfuryl))propanoic acid,[47] 10 mL of thionyl chloride, and 3 drops of pyridine in 100 mL of dry methylene chloride was heated at reflux for 4 h. The mixture was concentrated under reduced pressure, and the residue was dissolved in 100 mL of dry ether. This mixture was added dropwise to 520 mL of a 0.25 N ethereal solution of diazomethane at 5 °C. The resulting solution was stirred overnight and was then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using a 30% ether–hexane mixture as the eluent to give 8.6 g (88%) of 1-diazo-4-(2-(5-methylfuryl))-2-butanone (**11**) as a light yellow oil: IR (neat) 3110, 2930, 2110, 1650, 1580, 1375, 1340, 1225, 1150, 1105, 1030, and 790 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.23 (s, 3 H), 2.61 (t, 2 H, J = 7.0 Hz), 2.90 (t, 2 H, J = 7.0 Hz), 5.22 (s, 1 H), and 5.82 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.23, 23.29, 38.74, 54.29, 105.86, 105.97, 150.55, 152.17, and 193.19; UV (95% ethanol) 221 nm (ε 8750).

To a solution containing 712 mg of **11** in 400 mL of dry benzene under a nitrogen atmosphere was added 4 mg of rhodium acetate dimer. The solution was stirred for 3.5 h, during which time 88 mL of nitrogen gas was evolved. The solution was washed with several portions of a 1% sodium thiosulfate solution, water, and a saturated brine solution. The organic solution was then concentrated under reduced pressure, and the residue was purified by silica gel preparative thick-layer chromatography using a 40% ethyl acetate–hexane mixture as the eluent to give 522 mg (87%) of (*Z*)-1-(3-oxo-1-cyclopentenyl)-1-buten-3-one (**12**) as a pale yellow solid: mp 72–73 °C; IR (neat) 3500 (br), 2940, 1705, 1680, 1570, 1470, 1410, 1360, 1180, 1130, 1030, 980, and 880 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.29 (s, 3 H), 2.3–2.6 (m, 2 H), 2.7–3.0 (m, 2 H), 6.23 (s, 1 H), 6.32 (d, 1 H, J = 11.0 Hz), and 6.58 (d, 1 H, J = 11.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.08, 30.59, 35.20, 132.51, 133.13, 134.34, 170.18, 198.96, and 209.11; UV (95% ethanol) 273 nm (ε 9440). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.00; H, 6.73.

Rhodium Acetate Catalyzed Decomposition of 1-Diazo-5-(2-furyl)-2-pentanone (13). A stirred solution containing 4.0 g of 4-(2-furyl)butanoic acid,[48] 5 mL of thionyl chloride, and 3 drops of pyridine was heated at reflux for 3 h. The mixture was concentrated under reduced pressure, and the residue was dissolved in 100 mL of ether. This mixture was added dropwise to 240 mL of a 0.25 N ethereal solution of diazomethane at 5 °C. The solution was stirred overnight and was then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using a 30% ether–hexane solution as the eluent to give 3.14 g (68%) of 1-diazo-5-(2-furyl)-2-pentanone (**13**) as a yellow oil: IR (neat) 3110, 2940, 2100, 1640, 1510, 1475, 1145, 1000, 925, 805, and 735 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.93 (q, 2 H, J = 7.0 Hz), 2.27 (t, 2 H, J = 7.0 Hz), 2.64 (t, 2 H, J = 7.0 Hz), 5.21 (s, 1 H), 5.93 (d, 1 H, J = 2.0 Hz), 6.18 (dd, 1 H, J = 2.0 and 1.0 Hz), and 7.22 (d, 1 H, J = 1.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.35, 27.10, 39.41, 54.18, 105.24, 109.98, 140.89, 155.01, and 194.07; UV (95% ethanol) 268 (ε 6550) and 249 nm (7650).

To a solution containing 356 mg of **13** in 200 mL of dry benzene under a nitrogen atmosphere was added 4 mg of rhodium(II) acetate dimer. The solution was stirred for 3 h, during which time 45 mL of nitrogen gas was evolved. The mixture was washed with several portions of a 20% sodium thiosulfate solution, water, and a saturated brine solution and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 260 mg (87%) of a yellow oil, whose structure was assigned as *cis*-3-(3-oxo-1-cyclohexenyl)-2-propenal (**14**) on the basis of its spectral properties: IR (neat) 2950, 2870, 1670, 1410, 1335, 1245, 1190, 1115, 1070, 965, and 760 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.11 (q, 2 H, J = 7.0 Hz), 2.38 (t, 2 H, J = 7.0 Hz), 2.54 (t, 2 H, J = 7.0 Hz), 6.01 (s, 1 H), 6.04 (dd, 1 H, J = 11.0 and 7.0 Hz), 7.01 (d, 1 H, J = 11.0 Hz), and 9.98 (d, 1 H, J = 7.0 Hz).

The above material decomposed during silica gel chromatography and was converted into *trans*-3-(3-oxo-1-cyclohexenyl)-2-propenal (**15**) in the following manner. To a solution containing 260 mg of **14** in 50 mL of benzene was added 20 mg of iodine. The mixture was stirred for 6 h and was then washed with several portions of a 10% sodium thiosulfate solution, water, and a saturated brine solution. The mixture was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel preparative layer chromatography using a 30% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 210 mg (80%) of a yellow oil, whose structure was assigned as *trans*-3-(3-oxo-1-cyclohexenyl)-2-propenal (**15**) on the basis of its spectral properties: IR (neat) 2950, 1680, 1670, 1590, 1330, 1250, 1240, 1190, 1120, 1080, 900, 805, and 760 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.13 (q, 2 H, J = 7.0 Hz), 2.49 (t, 2 H, J = 7.0 Hz), 2.55 (t, 2 H, J = 7.0 Hz), 6.26 (s, 1 H), 6.48 (dd, 1 H, J = 16.0 and 7.0 Hz), 7.26 (d, 1 H, J = 16.0 Hz), and 9.75 (d, 1 H, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.94, 24.82, 37.54, 132.94, 133.28, 150.78, 153.13, and 192.45; UV (95% ethanol) 278 (ε 3810) and 255 nm (2920). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.81; H, 6.83.

Rhodium Acetate Catalyzed Reaction of 1-Diazo-3-(2-furyl)-2-propanone (16). A stirred solution containing 3.0 g of 2-furylacetic acid,[49] 5 mL of thionyl chloride, and 3 drops of pyridine in 100 mL of dry methylene chloride was heated at reflux for 3 h. The mixture was concentrated under reduced pressure, and the residue was dissolved in 100 mL of ether. This mixture was added dropwise to 240 mL of a 0.25 N ethereal solution of diazomethane at 5 °C. The solution was stirred overnight and was then concentrated under reduced pressure. The residue

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obtained was purified by silica gel column chromatography using a 30% ether–hexane mixture as the eluent to give 2.3 g of 1-diazo-3-(2-furyl)-2-propanone (**16**) as a yellow oil: IR (neat) 3110, 2925, 2115, 1645, 1515, 1480, 1440, 1150, 1020, 930, 810, and 730 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 3.68 (s, 2 H), 5.24 (s, 1 H), 6.22 (d, 1 H, J = 3.0 Hz), 6.37 (t, 1 H, J = 3.0 Hz), and 7.41 (d, 1 H, J = 3.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 40.04, 54.45, 108.37, 110.62, 142.18, 148.12, and 189.97.

To a solution containing 300 mg of **16** in 200 mL of dry benzene under a nitrogen atmosphere was added 4 mg of rhodium acetate dimer. The mixture was stirred for 4 h and was then concentrated under reduced pressure. The crude material obtained was purified by silica gel column chromatography using a 30% ether–hexane mixture as the eluent. The major fraction isolated contained 272 mg (68%) of 1-(2-furylacetyl)-2,4,6-cycloheptatriene (**18**), whose structure was assigned on the basis of its characteristic NMR spectrum: NMR (360 MHz, $CDCl_3$) δ 2.47 (t, 1 H, J = 5.8 Hz), 3.87 (s, 2 H), 4.96 (dd, 2 H, J = 7.6 Hz and 5.8 Hz), 6.20 (d, 1 H, J = 3.2 Hz), 6.30 (td, 2 H, J = 7.6 and 3.6 Hz), 6.33 (t, 1 H, J = 3.2 Hz), 6.55 (t, 2 H, J = 3.6 Hz), and 7.37 (d, 1 H, J = 3.2 Hz). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.71; H, 5.92.

Rhodium Acetate Catalyzed Reaction of 1-Diazo-4-(2-thienyl)-2-butanone (19). A solution containing 3.0 g of 3-(2-thienyl)propanoic acid[50] and 4.5 g of freshly distilled thionyl chloride in 100 mL of dry methylene chloride was heated at reflux for 5 h and was then concentrated under reduced pressure. The residue was dissolved in 100 mL of anhydrous ether, and this solution was added to another solution containing 1.9 g of diazomethane in 250 mL of ether at 5 °C. The resulting mixture was allowed to stand overnight. Removal of the solvent under reduced pressure followed by chromatography of the residue on a silica gel column using a 30% ether–hexane mixture as the eluent gave 2.50 g of 1-diazo-4-(2-thienyl)-2-butanone (**19**) (71%) as a yellow oil: IR (neat) 3110, 2940, 2110, 1645, 1440, 1380, 1330, 1150, 1100, 850, 830, and 700 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.69 (t, 2 H, J = 7.0 Hz), 3.13 (t, 2 H, J = 7.0 Hz), 5.24 (s, 1 H), 6.8–7.1 (m, 2 H), and 7.18 (dd, 1 H, J = 5.0 and 1.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 24.74, 41.80, 54.37, 123.18, 124.46, 126.59, 142.99, and 192.74.

To a stirred solution containing 300 mg of **19** in 100 mL of dry benzene under a nitrogen atmosphere was added 3 mg of rhodium(II) acetate dimer. The mixture was stirred at room temperature for 4 h and was then concentrated under reduced pressure. The resulting oil was assigned the structure of 3a,3b,5,6-tetrahydro-4*H*-cyclopenta[1,3]cyclopropa[1,2-*b*]thiophen-4-one (**20**) on the basis of its spectra properties: NMR ($CDCl_3$, 90 MHz) δ 1.16 (s, 1 H), 2.12 (br t, 2 H, J = 7.0 Hz), 2.44 (t, 1 H, J = 7.0 Hz), 2.56 (t, 1 H, J = 7.0 Hz), 2.92 (br t, 1 H, J = 2.0 Hz), 5.89 (dd, 1 H, J = 6.0 and 2.0 Hz), and 6.27 (d, 1 H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.71, 33.82, 33.99, 41.34, 49.94, 123.12, 129.08, and 211.58.

This material was found to undergo rearrangement during chromatography on silica gel or on treatment with a trace of acid. Preparative thick-layer chromatography on silica gel using a 30% ether–hexane mixture as the eluent gave 172 mg (68%) of 6,7-dihydrobenzo[*b*]thiophen-5(4*H*)-one (**21**) as a light yellow oil: IR (neat) 2930, 2860, 1720, 1450, 1350, 1290, 1110, 1090, 1050, 910, 840, and 710 cm^{-1}; NMR (CCl_4, 90 MHz) δ 2.60 (dt, 2 H, J = 7.0 and 1.0 Hz), 3.09 (br t, 2 H, J = 7.0 Hz), 3.38 (t, 2 H, J = 1.0 Hz), 6.64 (d, 1 H, J = 6.0 Hz), and 7.01 (d, 1 H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 23.90, 39.15, 40.38, 124.18, 126.98, 132.91, 133.78, and 208.78; UV (95% ethanol) 232 nm (ϵ 5500). Anal. Calcd for C_8H_8OS: C, 63.15; H, 5.30. Found: C, 62.98; H, 5.30.

Rhodium Catalyzed Rearrangement of 1-Diazo-4-(3-furyl)-2-butanone (22). To a stirred solution containing 3.0 g of 3-(3-furyl)propionic acid[51] in 55 mL of methylene chloride under a nitrogen atmosphere was added 5.0 g of freshly distilled thionyl chloride. The mixture was heated at reflux for 2 h, and then the solvent and excess thionyl chloride were removed under reduced pressure. The residue was dissolved in 25 mL of benzene, the solution was concentrated under reduced pressure, and 80 mL of anhydrous ether was added. The ethereal solution was cooled to 0 °C and was slowly added to a stirred solution containing 3.0 g of diazomethane in 250 mL of anhydrous ether at 0 °C. The solution was allowed to stand overnight and was then filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a 30% ether–hexane mixture as the eluent. The major fraction contained 1.91 g (62%) of 1-diazo-4-(3-furyl)-2-butanone (**22**) as a yellow oil: IR (neat) 3100, 2945, 2145, 1640, 1515, 1380, 1350, 1175, 1040, 890, and 800 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.64 (m, 4 H), 5.22 (s, 1 H), 6.24 (m, 1 H), and 7.28 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 19.78, 40.46, 54.39, 110.55, 123.34, 138.81, 142.64, and 193.64; UV (ethanol) 248 (ϵ 3770) and 272 nm (3770).

To a stirred solution containing 300 mg of **22** in 50 mL of benzene was added 3 mg of rhodium acetate dimer. The mixture was stirred for 2 h, filtered, and concentrated under reduced pressure, and the residue was purified by preparative silica gel thick-layer chromatography using a 20–40% ether–hexane mixture as the eluent to give 254 mg (88%) of (*Z*)-(4-oxo-2-cyclohexen-1-ylidene)acetaldehyde (**24**). The structure of this material was assigned on the basis of the following data: mp 71–72 °C; IR (KBr) 3050, 2950, 2700, 1627, 1560, 1420, 1350, 1260, 1150, 1120, and 860 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.65 (t, 2 H, J = 5.0 Hz), 2.90 (t, 2 H, J = 5.0 Hz), 6.14 (d, 1 H, J = 7.0 Hz), 6.29 (d, 1 H, J = 10.0 Hz), 8.01 (d, 1 H, J = 10.0 Hz), and 10.14 (d, 1 H, J = 7.0 Hz); UV (95% ethanol) 267 nm (ϵ 12 500); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 31.73 (t), 37.15 (t), 128.75 (d), 133.14 (d), 138.40 (d), 150.04 (s), 188.82 (d), and 197.14 (d). Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.36; H, 5.98.

Further support for this structure was obtained by its thermal behavior. A solution containing 544 mg of **24** in 30 mL of dry benzene was heated at 160 °C for 36 h. The solution was concentrated under reduced pressure, and the resulting yellow oil was purified by silica gel preparative thick-layer chromatography using a 40% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 473 mg (87%) of 4-hydroxyphenylacetaldehyde (**25**) as a pale yellow oil: IR (neat) 3400, 2840, 2720, 1720, 1615, 1600, 1520, 1445, 1360, 1225, and 830 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 3.59 (d, 2 H, J = 2.0 Hz), 6.0–6.6 (br s, 1 H), 6.76 (d, 2 H, J = 9.0 Hz), 6.98 (d, 2 H, J = 9.0 Hz), and 9.64 (t, 1 H, J = 2.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 49.58, 115.84, 123.47, 130.47, 155.10, and 200.08; UV (95% ethanol) 278 (ϵ 1350) and 282 nm (1240). Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.29; H, 5.93. This material was converted to a 2,4-dinitrophenylhydrazone derivative, which was recrystallized from ethanol–water to give a yellow solid, mp 183–184 °C (lit.[52] mp 183–184 °C).

Rhodium Acetate Catalyzed Reaction of 1-Diazo-4-(3-thienyl)-2-butanone (26). To a stirred solution containing 3.5 g of 3-(3-thienyl)propanoic acid[53] in 100 mL of dry methylene chloride was added 5 mL of freshly distilled thionyl chloride. The mixture was heated at reflux for 5 h and was then concentrated under reduced pressure. The residue was dissolved in 100 mL of ether, and this mixture was added to 220 mL of a 0.25 N ethereal solution of diazomethane at 5 °C. The resulting solution was stirred overnight, and the solvent was removed under reduced pressure to leave behind a yellow residue, which was purified by silica gel column chromatography using a 30% ether–hexane mixture as the eluent. The major fraction contained 2.50 g (69%) of 1-diazo-4-(3-thienyl)-2-butanone (**26**) as a yellow oil: IR (neat) 3110, 2920, 2110, 1690, 1440, 1380, 1330, 1140, 1100, 1020, 850, and 795 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.51 (t, 2 H, J = 7.0 Hz) 2.91 (t, 2 H, J = 7.0 Hz), 5.22 (s, 1 H), 6.8–7.0 (m, 2 H), and 7.12 (dd, 1 H, J =5.0 and 1.0 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 24.97, 40.85, 54.35, 120.31, 125.31, 127.66, 140.53, and 193.53.

A solution containing 720 mg of **26** and 4 mg of rhodium acetate dimer in 400 mL of dry benzene was stirred under a nitrogen atmosphere for 2 h. The mixture was washed with several portions of a 10% aqueous sodium cyanide solution, water, and a saturated brine solution. The solution was concentrated under reduced pressure to give 650 mg of a brown oil. This material was subjected to silica gel medium-pressure chromatography using a 30% eth-

(50) Blanchette, J. A.; Brown, E. V. *J. Am. Chem. Soc.* **1950**, *72*, 3414.
(51) See supplementary material for a description of the preparation of 3-(3-furyl)propionic acid.
(52) Boyer, F. *C. R. Seances Acad. Sci., Ser. C* **1976**, *264*, 1546.
(53) Mihailovic, M.; Tot, M. *J. Org. Chem.* **1948**, *13*, 315.

er–hexane mixture as the eluent. The first fraction isolated contained 380 mg (63%) of 4,5-dihydrobenzo[*b*]thiophen-6-(7*H*)-one (**27**) as a pale yellow oil: IR (neat) 3110, 2980, 2860, 1720, 1450, 1420, 1390, 1335, 1300, 1250, 1225, 1180, 980, and 710 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.62 (t, 2 H, J = 7.0 Hz), 3.01 (t, 2 H, J = 7.0 Hz), 3.60 (s, 2 H), 6.78 (d, 2 H, J = 5.0 Hz), and 7.11 (d, 2 H, J = 5.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 24.12, 38.64, 39.23, 123.85, 126.67, 131.57, 134.54, and 207.85; UV (95% ethanol) 236 nm (ϵ 3380). Anal. Calcd for C_8H_8OS: C, 63.15; H, 5.30. Found: C, 63.14; H, 5.30.

The second fraction isolated contained 60 mg (10%) of 6,7-dihydrobenzo[*c*]thiophen-5(4*H*)-one (**28**) as a pale yellow oil: IR (neat) 3100, 2960, 2920, 2860, 1720, 1450, 1415, 1390, 1330, 1280, 1250, 1160, 980, 870, 860, and 790 cm^{-1}; NMR (90 MHz, $CDCl_3$) 2.53 (t, 2 H, J = 7.0 Hz), 3.01 (t, 2 H, J = 7.0 Hz), 3.57 (s, 2 H), and 6.95 (br s, 2 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 23.70, 38.89, 41.05, 119.43, 120.38, 134.45, 136.71, and 209.44; UV (95% ethanol) 245 nm (ϵ 3600). Anal. Calcd for C_8H_8OS: C, 63.15; H, 5.30. Found: C, 62.90; H, 5.31.

Rhodium Acetate Catalyzed Rearrangement of 1-Diazo-4-(2-benzofuryl)-2-butanone (30). To a stirred solution containing 5.0 g of 3-(2-benzofuryl)propionic acid[54] in 100 mL of dry methylene chloride under a nitrogen atmosphere was added 10 mL of freshly distilled thionyl chloride. The mixture was heated at reflux for 3 h and was then concentrated under reduced pressure. The residue was dissolved in 100 mL of anhydrous ether, and this solution was added dropwise with stirring to 300 mL of a 0.25 M solution of diazomethane in ether at 0 °C. The mixture was stirred at room temperature overnight. Removal of the solvent under reduced pressure left a yellow oil, which was chromatographed on a silica gel column using a 20% ether–hexane mixture as the eluent. The major fraction isolated contained 3.96 g (71%) of 1-diazo-4-(2-benzofuryl)-2-butanone (**30**) as a light yellow solid: mp 49–50 °C; NMR ($CDCl_3$, 90 Hz) δ 2.20 (t, 2 H, J = 5.0 Hz), 3.13 (t, 2 H, J = 5.0 Hz), 5.20 (s, 1 H), 6.40 (s, 1 H), and 7.1–7.6 (m, 4 H); IR (KBr) 2135, 1625, 1455, 1385, 1250, 1180, 1155, 1010, 940, and 800 cm^{-1}; MS, m/e 214 (M^+), 186, 185, 158, 144, 131 (base), and 115; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 23.6, 38.13, 38.31, 102.65, 110.76, 120.48, 122.63, 123.46, 128.79, 154.75, 157.31, and 192.85; UV (95% ethanol) 250 nm (ϵ 12 500). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.04; H, 4.72; N, 12.98.

A solution containing 420 mg of **30** and 4.0 mg of rhodium acetate dimer in 200 mL of dry benzene was stirred in a base-washed flame-dried flask at room temperature for 1 h. The mixture was washed with three 50-mL portions of a 10% aqueous sodium cyanide solution, 50 mL of water, and 50 mL of a brine solution, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by preparative silica gel thick-layer chromatography using a 30% ether–hexane solution as the eluent to give 265 mg of 1,2,3a,3b-tetrahydro-3*H*-benzo[*b*]cyclopenta[2,3]cyclopropa[1,2-*d*]furan-3-one (**31**) (71%): mp 99–100 °C; IR (KBr) 3080, 2980, 1740, 1490, 1470, 1350, 1270, 1250, 1170, 1110, 1040, 1020, 920, 880, 830, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.25 (br s), 1.96 (dt, 1 H, J = 13.0 and 6.0 Hz), 2.08(dd, 1 H, J = 13.0 and 7.0 Hz), 2.60 (dd, 1 H, J = 7.0 and 6.0 Hz), 2.60 (d, 1 H, J = 6.0 Hz), 3.03 (br s, 1 H), and 6.2–7.3 (m, 4 H); MS, m/e 186 (M^+), 158 (base), 157, 144, 131, 130, 115, and 102; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.51, 32.71, 33.45, 35.01, 80.51, 110.76, 121.92, 124.70, 127.72, 128.23, 159.64, and 209.19. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.28; H, 5.44.

Acid-Catalyzed Reaction of 1,2,3a,3b-Tetrahydro-3*H*-benzo[*b*]cyclopenta[2,3]cyclopropa[1,2-*d*]furan-3-one (31). A solution containing 750 mg of **31** in 40 mL of ether was rapidly stirred with a 1% sulfuric acid solution for 30 min. The ether solution was dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by medium-pressure liquid chromatography on a silica gel column using a 10% acetone–hexane mixture as the eluent. The major fraction isolated contained 660 mg (88%) of a white solid, mp 100–101 °C, whose structure was assigned as 1,4-dihydrodibenzofuran-2(3*H*)-one (**33**) on the basis of the following data: IR (KBr) 2910, 1705, 1450, 1390, 1260, 1190, 1115, and 750 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.80 (t, 2 H, J = 6.0 Hz), 3.19 (tt, 2 H, J = 6.0 and 2.0 Hz), 3.53 (t, 2 H, J = 2.0 Hz), and 7.1–7.6 (m, 4 H); UV (95% ethanol) 247 (ϵ 5000), 277 (5000), and 284 nm (5000); MS, m/e 186 (M^+), 157, 149 (base), 131, and 115; ^{13}C NMR ($CDCl_3$, 20 MHz) δ 22.62, 35.40, 38.13, 110.57, 111.12, 118.44, 122.70, 124.06, 127.92, 151.19, 155.37, and 207.17. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.51; H, 5.45.

A solution connaining 310 mg of **31** in 40 mL of dry ether was rapidly stirred for 5 min with 25 mL of a 5% aqueous sulfuric acid solution. The aqueous solution was separated, and the organic layer was washed with water and a saturated sodium bicarbonate solution followed by a saturated brine solution. The solution was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left 270 mg of a white solid. Purification of this material by preparative silica gel chromatography using ether as the eluent gave 170 mg (50%) of a white crystalline solid, whose structure was assigned as 3,4,4a,9b-tetrahydro-4a-hydroxydibenzofuran-2(1*H*)-one (**34**): mp 102–103 °C; IR (KBr) 3300 (br), 1705, 1600, 1480, 1390, 1250, 1170, 1120, 1020, 990, 960, 910, and 770 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.2–2.5 (m, 6 H), 2.58 (dd, 0.5 H, J = 15.0 and 6.0 Hz), 2.96 (dd, 0.5 H, J = 15.0 and 6.0 Hz), 3.65 (br t, 1 H, J = 6.0 Hz), and 6.8–7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$, 90 MHz) δ 32.64, 33.17, 34.94, 35.12, 38.41, 42.86, 46.93, 50.18, 97.27, 109.07, 109.71, 116.24, 120.69, 121.49, 124.44, 128.32, 129.09, 129.35, 154.54, 157.09, 207.87, and 209.56; UV (95% ethanol) 278 (ϵ 2560) and 260 nm (sh, 1240); MS, m/e 204 (M^+), 174, 157, 146, 131, and 120. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.68; H, 5.96.

Thermal Rearrangement of 1,2,3a,3b-Tetrahydro-3*H*-benzo[*b*]cyclopenta[2,3]cyclopropa[1,2-*d*]furan-3-one (31). A solution containing 210 mg of **31** in 25 mL of toluene was heated at 180 °C in a sealed tube for 7 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure to leave behind a light yellow solid. This material was purified by preparative thick-layer chromatography on silica gel using a 50% ether–hexane mixture as the eluent. The major component contained 173 mg (82%) of a white solid, whose structure was assigned as 1,2-dihydrocyclopenta[*b*][1]benzopyran-3(9*H*)-one (**37**) on the basis of the following data: mp 193–194 °C; IR ($CHCl_3$) 3010, 1720, 1680, 1590, 1495, 1465, 1270, 1230, 1190, 1100, and 720 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.51 (s, 4 H), 3.72 (s, 2 H), and 6.9–7.2 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 24.92, 28.3, 32.69, 117.24, 117.62, 124.70, 129.26, 129.38, 144.39, 151.01, and 198.25; MS, m/e 186 (M^+), 185 (base), 160, 158, 154, 144, and 138; UV (95% ethanol) 277 (ϵ 2800) and 250 nm (1200). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.26; H, 5.33.

Unequivocal proof of the structure of **37** was established by an X-ray crystal-structure analysis. The crystals of **37** were triclinic with space group P_1, and the unit cell parameters were a = 6.7071 (3) Å, b = 7.4893 (4) Å, c = 10.0118 (5) Å, α = 108.856 (4)°, β = 95.003 (4)°, γ = 106.730 (3)°, Z = 2, and D_{calcd} = 1.38 g cm^{-3}. The structure was solved by direct methods and refined by blocked cascade matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms by using SHELXTL software. Convergence was achieved with R = 0.0366 for 1440 observations and 168 variables. The final positions and thermal parameters are given in Tables 1–3 of the supplementary material.

Rhodium Acetate Catalyzed Reaction of 1-Diazo-5-(2-benzofuryl)-2-pentanone (38). A stirred solution containing 5.0 g of 4-(2-benzofuryl)butanoic acid, 5 mL of thionyl chloride, and 3 drops of pyridine was heated at reflux for 3 h. The mixture was concentrated under reduced pressure, and the residue was dissolved in 100 mL of ether. This mixture was added dropwise to 240 mL of a 0.25 N ethereal solution of diazomethane at 5 °C. The resulting solution was stirred overnight and was then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography using a 30% ether–hexane solution as the eluent to give 4.3 g (78%) of 1-diazo-5-(2-benzofuryl)-2-pentanone (**38**) as a yellow oil: IR (neat) 3120, 2980, 2115, 1740, 1650, 1620, 1485, 1460, 1260, 1180, 1150, 1020, 950, and 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.09 (quin, 2 H, J = 7.0 Hz), 2.37 (t, 2 H, J = 7.0 Hz), 2.80 (t, 2 H, J = 7.0 Hz), 5.18 (s, 1 H), 7.0–7.2 (m, 2 H), and 7.3–7.6 (m, 2 H); ^{13}C NMR δ 22.62, 27.49, 39.21, 54.45, 102.41, 110.60, 120.16, 122.34, 123.14, 128.69,

(54) Foo Pan, B.; Wang, T. C. *Chem. Abstr.* **1963**, *58*, 133881a.

154.61, 158.07, and 194.12; UV (95% ethanol) 250 (ε 7700), 278 (2560), and 284 nm (2500).

To a solution containing 456 mg of **38** in 200 mL of dry benzene under a nitrogen atmosphere was added 4 mg of rhodium acetate dimer. The solution was stirred for 1 h, during which time 45 mL of nitrogen had been evolved. The mixture was washed with several portions of a 10% sodium cyanide solution, water, and a saturated brine solution and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the resulting clear oil was purified by silica gel preparative layer chromatography using a 20% ether–hexane mixture as the eluent. The first fraction isolated contained 150 mg (38%) of a white solid, whose structure was assigned as cyclopropane **39**: mp 59–60 °C; IR (KBr) 3015, 2970, 1720, 1605, 1590, 1455, 1375, 1255, 1180, 1100, 950, 805, 750, and 710 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 1.45 (d, 1 H, J = 3.0 Hz), 1.83 (m, 2 H), 2.27 (td, 2 H, J = 7.0 and 1.0 Hz), 2.51 (dd, 2 H, J = 10.0 and 7.0 Hz), 3.25 (d, 1 H, J = 3.0 Hz), and 6.7–7.5 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.46, 23.97, 32.06, 36.05, 36.20, 75.80, 110.42, 121.07, 123.98, 127.98, 128.65, 158.65, and 204.68; UV (95% ethanol) 282 (ε 4970) and 232 nm (4400). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.83; H, 6.10.

The second fraction isolated contained 310 mg (56%) of a light yellow oil, whose structure was assigned as 1-oxo-4-(2-benzofuryl)-1-(1-(2,4,6-cycloheptatrienyl))butane (**40**) on the basis of its characteristic spectral properties: IR (neat) 3060, 2960, 2890, 1690, 1620, 1600, 1480, 1470, 1360, 1330, 1290, 1230, 1130, 1100, 1020, 920, 880, 840, 760, and 720 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 2.09 (quin, 2 H, J = 7.2 Hz), 2.39 (t, 1 H, J = 5.8 Hz), 2.66 (t, 2 H, J = 7.2 Hz), 2.82 (t, 2 H, J = 7.2 Hz), 5.02 (dd, 2 H, J = 8.2 and 5.8 Hz), 6.29 (td, 2 H, J = 8.2 and 3.6 Hz), 6.40 (s, 1 H), 6.56 (t, 2 H, J = 3.6 Hz), 7.17 (t, 1 H, J = 6.8 Hz), 7.21 (t, 1 H, J = 6.8 Hz), 7.40 (d, 1 H, J = 6.8 Hz), and 7.47 (d, 1 H, J = 6.8 Hz). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.74; H, 6.43.

Further support for the structure of **39** was obtained from its acid-catalyzed behavior. To a stirred solution containing 80 mg of **39** in 10 mL of dry benzene at room temperature was added 10 mg of *p*-toluenesulfonic acid. The mixture was stirred for 6 h at room temperature and was then washed with 25 mL of water, a saturated sodium bicarbonate solution, and a brine solution. The solution was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by silica gel preparative thick-layer chromatography using a 30% ether–hexane solution as the eluent to give 58 mg (73%) of cycloheptabenzofuranone **41** as a clear oil. The structure was assigned on the basis of its spectral properties: IR (neat) 3060, 2960, 1715, 1460, 1340, 1280, 1230, 1115, 1100, 855, and 750 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 2.23 (quin, 2 H, J = 7.0 Hz), 2.73 (t, 2 H, J = 7.0 Hz), 3.07 (t, 2 H, J = 7.0 Hz), 3.77 (br s, 2 H), 7.20–7.29 (m, 2 H), and 7.36–7.43 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.03, 28.34, 37.21, 43.17, 106.52, 110.63, 118.18, 122.42, 123.84, 129.02, 153.25, 154.18, and 207.49; UV (95% ethanol) 284 (ε 3070), 278 (3080), and 250 nm (7740). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.07. Found: C, 78.12; H, 6.07.

Preparation of 1-Diazo-4-(3-benzofuryl)-2-butanone (42). A stirred solution containing 2.5 g of 3-formylbenzofuran[55] and 2.6 g of dry malonic acid in 20 mL of dry pyridine was heated at 45 °C for 12 h. The temperature was raised to 100 °C for approximately 2.5 h until gas evolution had ceased. The mixture was acidified with dilute hydrochloric acid and was extracted with three 50-mL portions of ether. The combined ether extracts were washed with 50 mL of water and 50 mL of a saturated sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure to give 2.83 g of crude 3-(3-benzofuryl)acrylic acid (87%). Recrystallization from 95% ethanol gave rise to a pure sample: mp 186–187 °C; IR (KBr) 2900 (br), 1660, 1640, 1550, 1340, 1130, 990, and 750 cm^{-1}; NMR (DMSO-d_6, 90 MHz) δ 6.55 (d, 1 H, J = 16.0 Hz), 7.3–7.5 (m, 2 H), 7.6–7.8 (m, 1 H), 7.76 (d, 1 H, J = 16.0 Hz), and 8.50 (s, 1 H). Anal. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 70.04; H, 4.34.

A solution conaining 5.0 g of the above acid and 500 mg of a 5% palladium on charcoal catalyst in 60 mL of 95% ethanol was stirred in an atmospheric hydrogenation apparatus until 604 mL of hydrogen had been absorbed. The mixture was filtered through a Celite pad and concentrated under reduced pressure to give 5.02 g of 3-(3-benzofuryl)propionic acid (99%). Recrystallization from a 10% ethanol–water mixture gave a pure sample: mp 110–111 °C; IR (KBr) 3000, 2950, 1725, 1600, 1450, 1390, 1300, 1270, 1230, 1150, 1090, and 750 cm^{-1}; NMR (DMSO-d_6, 90 MHz) δ 2.64 (t, 2 H, J = 7.0 Hz), 2.93 (t, 2 H, J = 7.0 Hz), 7.1–7.7 (m, 4 H), and 7.75 (s, 1 H); MS, m/e 190 (M^+), 145, 131 (base), 125, and 103.

To a stirred solution containing 3.5 g of this acid in 75 mL of dry methylene chloride under a nitrogen atmosphere was added 6.5 g of freshly distilled thionyl chloride. The mixture was heated at reflux for 4 h and was then concentrated under reduced pressure. The residue was dissolved in 75 mL of anhydrous ether, and the solution was added dropwise at 5 °C to a stirred solution containing 2.3 g of diazomethane in 150 mL of anhydrous ether. The mixture was allowed to stand overnight at 0 °C, filtered, and concentrated under reduced pressure to give a brown oil, which was purified by preparative silica gel thick-layer chromatography using a 20–40% ether–hexane solution as the eluent. The major fraction isolated contained 3.03 g of a light yellow oil (76%), which was identified as 1-diazo-4-(3-benzofuryl)-2-butanone (**42**) on the basis of its spectral properties: IR (neat) 3100, 2930, 2120, 1640, 1450, 1370, 1190, 1140, 1100, 1020, 870, and 760 cm^{-1}; NMR (CCl_4, 90 MHz) δ 2.39 (t, 2 H, J = 7.0 Hz), 2.87 (t, 2 H, J = 7.0 Hz), 5.09 (s, 1 H), 7.2–7.6 (m, 4 H), and 7.34 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 18.63, 39.73, 54.58, 111.37, 118.86, 119.22, 122.26, 124.27, 127.63, 141.32, 155.24, and 193.33; UV (95% ethanol) 248 (ε 13170), 276 (5850), and 283 nm (4880).

Rhodium Catalyzed Rearrangement of 1-Diazo-4-(3-benzofuryl)-2-butanone (42). A solution containing 172 mg of **42** and 1.72 mg of rhodium(II) acetate dimer in 80 mL of dry benzene was stirred at room temperature for approximately 3 h until nitrogen evolution had ceased. The mixture was washed with two 50-mL portions of a 10% aqueous sodium cyanide solution and 50 mL of a saturated aqueous sodium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure. The crude oil was purified by preparative silica gel thick-layer chromatography using a 40% ether–hexane mixture as the eluent to give 140 mg of a white crystalline solid, whose structure was assigned as 1,2,3a,3b-tetrahydro-3*H*-benzo[*b*]-cyclopenta[1,3]cyclopropa[1,2-*d*]furan-3-one (**43**) on the basis of its spectroscopic properties: mp 90–91 °C; IR (KBr) 3050, 2930, 1725, 1620, 1600, 1460, 1200, 1080, 1060, 1030, and 930 cm^{-1}; UV (95% ethanol) 250 (ε 6900), 277 (3500), and 284 nm (3500); NMR ($CDCl_3$, 360 MHz) δ 1.32 (s, 1 H), 2.13 (ddd, 1 H, J = 18.0, 12.0, and 7.5 Hz), 2.47 (dd, 1 H, J = 18.0 and 9.0 Hz), 2.55 (dd, 1 H, J = 12.0 and 7.5 Hz), 2.92 (t, 1 H, J = 12.0 and 9.0 Hz), 5.02 (s, 1 H), 6.89 (d, 1 H, J = 7.0 Hz), 6.99 (t, 1 H, J = 7.0 Hz), 7.18 (t, 1 H, J = 7.0 Hz), and 7.37 (d, 1 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.39, 35.57, 35.96, 43.04, 70.61, 110.57, 121.36, 122.44, 128.13, 128.20, 159.63, and 209.02. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.15; H, 5.55.

A solution containing 250 mg of **43** and 10 mg of *p*-toluenesulfonic acid in 134 mL of dry benzene was stirred for 6 h at 25 °C. The organic solution was washed with a saturated sodium bicarbonate solution, followed by water and a saturated brine solution. The solution was concentrated under reduced pressu ɜ, and the residue was purified by silica gel preparative thick-layer chromatography to give 213 mg (92%) of 1,4-dihydrodibenzofuran-3(2*H*)-one (**44**) as a white crystalline solid: mp 86–87 °C; IR (KBr) 3060, 2910, 2840, 1730, 1650, 1485, 1460, 1390, 1340, 1305, 1280, 1180, 1135, 1020, 850, and 765 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 2.77 (t, 2 H, J = 6.8 Hz), 2.99 (tt, 2 H, J = 6.8 and 1.8 Hz), 3.62 (t, 2 H, J = 1.8 Hz), 7.2–7.3 (m, 2 H), and 7.4–7.5 (m, 2 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 18.01, 38.67, 38.90, 111.09, 112.53, 118.56, 122.65, 123.85, 127.31, 149.22, 155.25, and 205.84; UV (95% ethanol) 252 (ε 11500), 284 (3130), 278 (2770), and 252 nm (12000); MS, m/e 186 (M^+), 158, 157, 145, 144 (base), 131, and 115. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.28; H, 5.41.

The thermal rearrangement of **43** was also studied. A solution containing 230 mg of **43** in 30 mL of dry benzene was heated at 110 °C for 13 h. The solution was concentrated under reduced pressure, and the resulting residue was dissolved in 25 mL of a 10% aqueous potassium hydroxide solution. This solution was

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washed with ether, acidified with concentrated hydrochloric acid, and extracted with ether. The combined ether extracts were concentrated under reduced pressure to give 197 mg of a tan solid. This material was purified by silica gel preparative thick-layer chromatography using a 40% ethyl acetate–hexane solution as the eluent to give 189 mg (82%) of 2,4'-biphenyldiol (**46**): mp 162–163 °C (lit.[56] mp 162–163 °C); IR (KBr) 3490 (br), 3360 (br), 1600, 1525, 1500, 1450, 1425, 1390, 1360, 1335, 1280, 1250, 1200, 1180, 1110, 840, and 770 cm^{-1}; NMR (360 MHz, $CDCl_3$) δ 4.86 (br s, 1 H), 5.13 (br s, 1 H), 6.92–7.00 (m, 4 H), 7.18–7.25 (m, 2 H), and 7.33–7.38 (m, 2 H); UV (95% ethanol) 291 (ϵ 2450) and 256 nm (3320). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.08; H, 5.26.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health. Use of the high field NMR spectrometer used in these studies was made possible through a NSF equipment grant.

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Registry No. **3**, 54487-06-8; **3** (acid), 935-13-7; **3** (acid chloride), 54536-91-3; **5**, 54487-07-9; **8**, 105456-74-4; **9**, 117040-60-5; **10**, 117040-61-6; **11**, 105456-75-5; **11** (acid), 1456-08-2; **12**, 117040-62-7; **13**, 105456-77-7; **13** (acid), 92038-98-7; **14**, 113541-28-9; **15**, 113541-29-0; **16**, 117040-63-8; **16** (acid), 2745-26-8; **18**, 117040-64-9; **19**, 59554-98-2; **19** (acid), 5928-51-8; **20**, 117040-65-0; **21**, 58095-45-7; **22**, 105456-82-4; **22** (acid), 90048-04-7; **24**, 105456-83-5; **25**, 7339-87-9; **25** (2,4-dinitrophenyl hydrazone), 107455-76-5; **26**, 117040-66-1; **26** (acid), 16378-06-6; **27**, 117040-67-2; **28**, 117040-68-3; **30**, 10546-79-9; **30** (acid), 21683-86-3; **31**, 105456-80-2; **33**, 69888-44-4; **34**, 117040-69-4; **37**, 105456-81-3; **38**, 117040-70-7; **38** (acid), 91962-99-1; **39**, 117040-71-8; **40**, 117040-72-9; **41**, 117040-73-0; **42**, 105456-84-6; **42** (acid), 15433-88-2; **43**, 105456-85-7; **44**, 105456-86-8; **46**, 611-62-1; $Rh_2(OAc)_4$, 15956-28-2; $CH_2(CO_2H)_2$, 141-82-2; 3-formylbenzofuran, 4687-25-6; 3-(3-benzofuryl)acrylic acid, 114949-09-6.

Supplementary Material Available: Experimental details for the preparation of 3-(3-furyl)propionic acid as well as the final positions and thermal parameters of the X-ray analysis of 1,2-dihydrocyclopenta[*b*][1]benzopyran-3(9*H*)-one (**37**) (5 pages). Ordering information is given on any current masthead page.

Selectivities in the Addition of Radicals Generated from Derivatives of 2-Bromomalonic Acid to Alkene Pairs[1]

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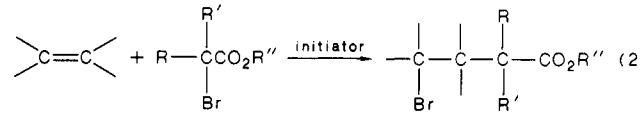
Direct competitions between 1-octene and three symmetrical tetraalkylethylenes for free radicals generated from derivatives of 2-bromomalonic acid were investigated. Despite the fact that these radicals are all electrophilic in nature, the less electron rich terminal alkene undergoes preferred reaction in many instances. This is principally caused by the steric demands of the attacking radical. Variation in both steric and electronic factors, however, lead to a wide range of relative reactivities.

The last decade has observed a renewed interest in the development of free-radical reactions suitable for synthetic purposes. The formation of carbon–carbon bonds by the addition of carbon free radicals to unsaturated molecules has received particular attention.[2] Several of these processes show stereospecificity as well as the expected regiospecificity and have been utilized in the synthesis of complex natural products.[3,4] Despite this resurgence of interest, and the fact that such radical additions were initially characterized over 50 years ago by Kharasch and his co-workers,[5] the factor(s) mainly responsible for the regiochemistry of the rate-determining step (eq 1) still remain controversial. Is this preferred addition to the

$$RCH{=}CH_2 + Z^{\bullet} \rightarrow R\dot{C}HCH_2Z \qquad (1)$$

terminal end of the double bond associated with the electronic factors that make a secondary radical more stable than its primary counterpart, or, rather, is this the result of steric factors that make the terminal position more accessible? In all probability both must play some role. Tedder and Walton have suggested that several factors are operative in this process.[6] This view has been further substantiated by Giese[7] and by Münger and Fischer.[8]

Recent results obtained in this laboratory were also relevant to this question.[9] The esters of 2-bromo carboxylic acids add readily to alkenes via a radical pathway (eq 2).[10] In competitive additions between 1-methyl-



cyclohexene and 1-octene for a series of carbethoxyalkyl radicals, it was observed that the former compound always underwent preferential reaction. This was somewhat surprising as most of these carbethoxyalkyl radicals show modest nucleophilic character.[9] These results were rationalized in terms of the relative position of the transition

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